CHAPTER I
INTRODUCTION

The semiconducting ceramics, such as ferroelectrics, antiferroelectrics, superconductor and piezoelectric products, show great potentials for using as sensors, actuators, transducers, electro-optic devices, thermistors, microelectro mechanical system (MEMS) applications (micromotors, microvalves, micropumps), PTC (positive temperature coefficient), acoustic transducer, binary ferroelectric memory, resistors and capacitors because of their good properties on dielectricity, pyrolectricity and piezoelectricity (Fang *et al.*1999; Lobmann *et al.*1995; Paris *et al.* 1998; YXL, 1993). The most common and well-known electrical and semicon ducting ceramic materials are lead titanate ($PbTiO_3$), lead zirconate ($PbZrO_3$), lead zirconate titanate (PZT or $Pb(Zr,Ti)O_3$) and lead/lanthanum zirconate titanate (PLZT or $(Pb,La)(Zr,Ti)O_3$). Many processes to produce these semiconducting ceramic materials include the sol-gel method, the chemical co-precipitation, the hydrothermal synthesis, the traditional solid state reaction of mixed oxides, the molten salt preparation, the solvothermal synthesis, the emulsion technique, and the complex polymerization (YXL,1993; Fang *et al.*2002; Hermandez *et al.*2002; Bersani *et al.*1995; Gurkovich *et al.*1982). The sol-gel process has an advantage over others in producing various shapes during the gel-state at low processing temperatures, e.g., monoliths, films, fibers and monosized powders along with compositional and microstructural controls (Brinker, 1990). For conventional processes of producing semiconducting ceramics, the raw starting materials from metal alkoxide precursors require very high purity, but they are expensive and extremely moisture sensitive (Brinker, 1990).

Ferroelectric crystals necessarily possess both pyroelectric and piezoelectric properties. Many lose these polar properties at the transition or the Curie temperature T_c. A nonpolar phase above T_c is called paraelectric phase. Lead titanate and lead zirconate titanate are kinds of ferroelectric materials which have electric dipole moment which can be spontaneously polarized with reversibility. Furthermore, ferroelectric can be used as biosensor such as piezo-sensing devices and biosensors for urea, glucose, DNA, immune cholesterol (Brinker,1990).

Lead zirconate is an antiferroelectric material having a non-permanent electric dipole moment whose complete or partial realignment can be reversible under appropriate conditions. Lead zirconate can show a phase switching from the antiferroelectric phase to the ferroelectric phase by applying electric field or raising temperature.

The methods required for the synthesis of alkoxy derivatives of an element generally depend on its electronegativity and electron configuration. The chelating nature of the glycol and the coordinative saturation achieved by the central atoms in the final products appear to be the main factor for their hydrolytic stability to retard the hydrolysis and condensation reaction rates in order to form homogeneous gels rather than precipitates (Kakihana *et al.*1997). Other work reported metallogly colates formed from alkaline glycol such as aluminium, silicon, titanium, and magnesium-aluminium (Yang *et al.*2001; Day *et al.* 1996; Brinker *et al.*1986). Specifically, (Archer *et al.* 1996) studied the role of precursor segregation in the formation of the perovskite phase $PbTiO_3$ using either lead oxy glycolate $Pb(OCH_2CH_2O)_2$ or lead phenoxy glycolate compounds. The lead precursors were synthesized by refluxing the lead carbonate with an appropriate carboxylic acid in water.

From previous studies, the sol-gel process appears to be the mildest method to produce lead titanate, lead zirconate, lead zirconate titanate. In an all-alkoxide sol-gel process, alkoxides of the constituent elements show different reactivities toward water so that the preparation of multicomponent homogeneous systems is difficult. The high cost of the alkoxide reagents and the need to work under inert atmospheres are major disadvantages of this system. Inorganic and organic salts have also been used for the sol-gel processing of multicomponent systems when the use of constituent alkoxides become difficult or unnecessary. Many researches (Wongkasemjit *et al.* 2001) have demonstrated that using the Oxide One Pot Synthesis (OOPS) process, moisture stable metal alkoxides can be successfully synthesized. Therefore, the aim of this study is to synthesize high purity lead titanate, lead zirconate and lead zirconate titanate (PZT) via the sol-gel process using lead glycolate, titanium glycolate and sodium tris (glycozirconate) precursors from the OOPS process. We also investigate the influence of calcination temperature and time on physical and chemical properties; i.e., morphology, phase transformation, and electrical properties.

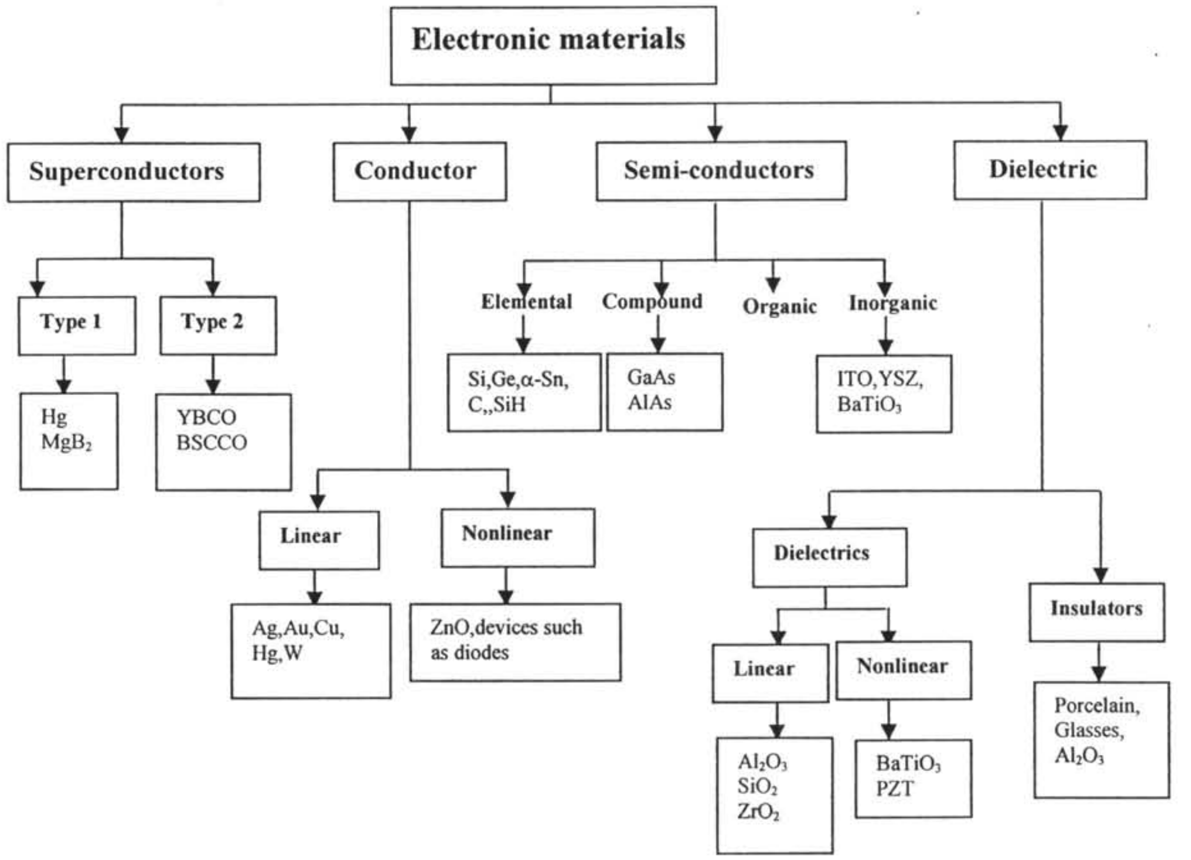

Figure 1.1 Classification of technologically useful electronic materials.

As stated, the aim of this work is to prepare lead glycolate precursor, lead titanate ($PbTiO_3$), lead zirconate ($PbZrO_3$), and lead zirconate titanate (PZT/ $Pb(Zr_xTi_{1-x})O_3$) which are ferro-antiferro-piezo electric materials with high purity, homogeneous dispersion, at reduced calcination temperature and time, along with good electrical properties. The lead glycolate precursor was synthesized by using the OOPS process. The lead titanate, lead zirconate and lead zirconate titanate were then prepared by using the synthesized precursors and the sol-gel process.

The scope of this research work is as follow;

1. To investigate the optimal conditions for the preparation lead glycolate precursor by the OOPS process.

2. To investigate the optimal conditions for the preparation of lead titanate, lead zirconate and lead zirconate titanate using lead glycolate, titanium glycolate and sodium tris (glycozirconate) as the precursors. The effects of this study include:
   - Effect of molar ratio
   - Effect of calcination temperature
   - Effect of reaction time
   - Effect of sol-gel transition
3. To characterize their electrical properties.

In this study, the sol-gel process was employed to hydrolyze and condense alkoxide precursors because of its product homogeneity and to control physical and chemical characteristics (i.e. morphology, distribution, phase transformation, electrical properties). Thus, lead titanate, lead zirconate, lead zirconate titanate (PZT) synthesized via the sol-gel process are expected to have high quality and improved electrical properties.